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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. 12707 P03
First inventor or Application Identifier Daniele Casalini
Title SURFACE-COATED HARD MATERIAL, PRODUCTION
Express Mail Label No. EL377526025US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

- ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)
- ☒ Specification [Total Pages 21]
(preferred arrangement set forth below)
 - Descriptive title of the Invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to Microfiche Appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
- ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 3]
- Oath or Declaration [Total Pages 24]
 - ☐ Newly executed (original or copy)
 - ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 16 completed)
 - ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

- ☐ Microfiche Computer Program (Appendix)
- Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
 - ☐ Computer Readable Copy
 - ☐ Paper Copy (identical to computer copy)
 - ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

- ☐ Assignment Papers (cover sheet & document(s))
- ☐ 37 C.F.R. §3.73(b) Statement of Power of Attorney (when there is an assignee)
- ☒ English Translation Document (if applicable)
- ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
- ☒ Preliminary Amendment
- ☒ Return Receipt Postcard (MPEP 503) (Should be specifically itemized)
- ☐ * Small Entity Statement(s) filed in prior application, Status still proper and desired (PTO/SB/09-12)
- ☒ Certified Copy of Priority Document(s) (if foreign priority is claimed)
- ☒ Other: filed under provisions of 35 USC 111 & 37 CFR 1.53(b), (d) and without the oath of 35 USC 115

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: _____
Prior application information: Examiner _____ Group / Art Unit: _____

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.


17. CORRESPONDENCE ADDRESS

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12707 P03
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7/17/00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Daniele CASALINI, a citizen of Italy

For:: SURFACE-COATED HARD MATERIAL, PRODUCTION METHOD FOR THIS,
AND USE OF THE SAME

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TO: Honorable Assistant Commissioner of Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

This amendment is presented with the application as filed to reduce the number of (deemed) claims and filing fee and for adjustment with U.S. format.

CLAIMS

Claim 4, line 1, change "; one of claims 1 to 4" to -- claim 1 --.

Claim 6, line, after "is" insert -- selected from the group consisting of -- and change "and/or" to -- and --.

Claim 9, lines 1-2, change "one of the claims 1 to 8" to -- claim 1 --.

Claim 12, lines 1-2, change "one of the claims 1 to 11" to -- claim 1 --.

Claim 16, line 1, change "one of the claims 12-15" to -- claim 12 --.

Claim 17, change "one of the claims 12-16" to -- claim 12 --.

Claim 19, lines 1-2, change "one of the claims 1 to 11" to -- claim 1 -- and in line 3, add at the beginning -- a material selected from the class consisting of -- and in the last line change "and/or" to -- and --.

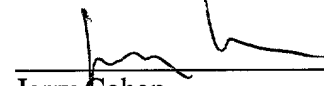
Claim 20, lines 1 to 2, change "one of the claims 1 to 11" to -- claim 11 --.

If any questions remain, please call Applicant's attorney, collect, at the number given above. If any sums are owed due to claim adjustments, please debit or credit Deposit Account 03-2410, order 12707-3.

Respectfully submitted,
DANIELE CASALINI, Applicant

Dated: July 17, 2000

By:



Jerry Cohen
Reg. No. 20,522
Attorney for Applicant

A Surface-Coated Hard Material, Production Method for This,
and Use of the Same

The present invention relates to a surface-coated hard
5 [mechanically resistant] material as defined generically in
Claim 1, a production method for this as defined in Claim 12,
and use of the same as defined in Claim 19.

10 It is known that coats of lacquer applied to flooring laminates,
genuine wood laminates, parquet, furniture, or to wood or
plastic panels in general can have resin added to them in order
to make them resistant to wear. When this is done, lacquer
systems based on phenol, melamine, aldehyde, formaldehyde, urea,
epoxy, polyester and/or polyurethane resins are used. Preferred
15 lacquer systems are the melamine resins. Because of its
hardness, transparency, inertness, and availability, aluminum
oxide or alumina products in the form of fused corundum,
sintered corundum, monocrystalline corundum and/or calcined or
sintered alumina such as plate-like alumina are preferred for
20 increasing the wear-resistance of the coatings.

EP 0 732 449 A1 discloses a method for producing wear-resistant
laminates, in which the surface of the resin-impregnated paper
that is used during the production process is coated with a
25 mixture consisting of melamine resin, cellulose fibres, corundum
as the hard material, additives and water, and is dried to a
specific residual moisture content. The resin-impregnated paper

is processed within the laminate in the usual way. After the laminate has been pressed and the melamine resin has hardened, the corundum is firmly bonded into the resin layer, the wear resistance of which is greatly increased because of the hardness of the corundum. DE 195 29 987 A1 discloses a method for producing highly wear-resistant lacquer coatings on a solid carrier, when wear-reducing material is either scattered directly onto the surface of the carrier and then covered with a synthetic-resin lacquer (acrylate resin, polyester resin, or polyurethane resin lacquer), or the wear-reducing agent is scattered onto the surface of the carrier that is already coated with lacquer. Generally speaking, when this is done, the wear-reducing effect of the resin increases as the grain size increases and as the degree to which the lacquer coating is filled increases. The maximum grain size that can be used, which is, at the same time, the optimal size, is determined by the thickness of the lacquer coating. However, the optimal degree of filling does not correspond to the possible maximum but is limited by the simultaneous demand for the highest possible degree of transparency of the lacquer coating. The subsequent pressing and hardening of the lacquer is effected by using known technology. One additional variant that is available in particular for laminates is that a transparent overlay paper that incorporates the appropriate resin is impregnated with lacquer then pressed onto the decorative layer and hardened. It is preferred that corundum be used as the wear-reducing agent.

Synthetic corundum is usually produced in an arc furnace, when the starting material--alumina or bauxite--is smelted at approximately 2000°C. In this process, the product is in the form of large blocks weighing several tonnes, and after cooling these are crushed and then processed into granular material. Typical areas of use for granular corundum, which is available in the most varied grades and grain sizes ranging from a few millimeters to several micrometers, are as grinding agents and refractory products. Because of its brittle-fracture behaviour, when the corundum is ground this results in a markedly fissured surface with many edge dislocations, micro-edges, grooving, and cracks. Similar grain surfaces with additional pores also seen in sintered or calcined alumina, particularly if they have been previously subjected to a grinding process. Grain surfaces of this kind display a high degree of capillarity with respect to low-viscosity liquids. Such grain characteristics have been found to be disadvantageous when processing aluminum oxide to form wear-resistant coatings.

According to the current state of the art, today, a wear-resistant lacquer coating is produced by a single application of the wear-reducing lacquer to which the hard granular material has already been mixed, subsequent drying, and pressing. When this is done, the particles of hard material lie, in part, directly on the surface of the protective coating so that, for example, dyes or other coloured liquids with a high level of creepage penetrate irreversibly into the micro-capillaries of

these hard material particles thereby causing patches that cannot be removed from the laminate or lacquer surface. Attempts that have been made to avoid this effect by using low-viscosity lacquer systems that cover the whole of the granular material surface have been unsuccessful, since a minimum degree of viscosity is needed in order to achieve the desired thickness of the lacquer coating.

A further disadvantage of the markedly fissured surfaces of the hard granular material that cannot be completely wetted with lacquer is the fact that light is scattered diffusely on the above-discussed micro-edges, cracks, and edged displacements so that the transparency of the lacquer coating that is filled with aluminum oxide is degraded. However, a high degree of transparency is one of the most important criteria for these coatings, which are frequently used in applications in which the visual effect plays a major role. In addition to this, small air bubbles can accumulate on these micro-edges and cracks, and this causes an additional diffuse scattering of the light, with the result that transparency is still further degraded.

Thus, it is the objective of the present invention to describe granular hard material that does not suffer from the disadvantages described heretofore.

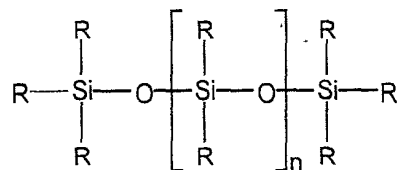
This objective has been achieved with a hard material having the features described in Claim 1, by a method for the production of

this as described in Claim 13, as well as by the use of this material as described in Claims 19 and 20.

Advantageous variations of the present invention are set out in the secondary Claims.

This is realized concretely by a hard material with a hardness $(HV_{0.2}) \geq 10$ GPa, the surface of which is covered with a polysiloxane coating.

It is preferred that the treatment of the hard material be effected with a polysiloxane solution of the following formula:



wherein the R radical can in each instance be a hydrogen, alkyl and/or phenyl group, and n stands for an integer from 1 to 100. Especially good results are achieved if the organic R radical is a methyl group.

Surface treatments or coatings with particles of hard materials have been known for a considerable time and are used for the most varied purposes. For instance, EP 0 387 748 describes a hydrophobically coated grinding grain that is based on corundum and/or silicon carbide, the surface of which is treated with highly dispersed hydrophobic silicon oxide so that the strength

with which the grain is bonded into the synthetic resin is improved. Similarly, according to EP 304 616, an improvement of the bonding of grinding grains in a plastic resin system is achieved by surface treatment with hygroscopic and/or hydrophobic substances. In addition, this treatment entails the additional effect that granular material treated in this way disperses better in the electrostatic field.

It is also usual to coat the grains with a binder and a pigment in order to increase the surface area of the grain, thereby once again enhancing the way in which the grain is bound in when grinding agents are manufactured. This coating also has the effect of simultaneously improving the dispersability of the granular material. However, none of the above treatments can compensate for the disadvantages of aluminum oxide when it is used in lacquer coatings or laminates (a high degree of capillarity as compared to low-viscosity liquids and diffuse dispersion of the light).

On the other hand, if one mixes hard granular material based on aluminum oxide with polysiloxanes or corresponding emulsions or solutions, because of the outstanding creep behaviour of the polysiloxanes one achieves complete coating of the surface of the individual grains, when the micro-edges, cracks, grooves, and offset edges are covered over or filled so that low-viscosity liquids can no longer penetrate into the grain and

there is no longer any diffuse dispersion of light on the cracks or edges.

Hard material based on aluminum oxide can be electro-smelted corundum, monocrystalline corundum, sintered corundum, tabular alumina, calcined or sintered alumina products, such as plate-form alumina, or mixtures of these. There are no restrictions as to the size of the grain for the hard material that is to be used. Depending on the requirement and the application, both micro- as well as macro-granular material can be treated according to the present invention. However, the hardness of the hard grains should have a minimum value of 10 GPa, preferably 15 GPa, in order to provide adequate protection against wear. The processing itself is effected in the known manner by spraying on an appropriate polysiloxane solution or emulsion or by mixing the hard material with a polysiloxane solution or emulsion in suitable mixers (tumbling mixers, rotary mixers, staggered-baffle drum mixers, and/or intensive mixers). Depending on the moisture content of the starting granular material, it has been found advantageous to subject the material to heat treatment in a temperature range between 100°C and 600°C immediately prior to the coating process, in order to eliminate any moisture that is adhering to the surface, including the pores and cracks. The quantity and concentration of the polysiloxane solution must be so selected that the complete surface of each individual grain is covered once it has been treated. The finer the grain size of the material that is to be

treated the greater will be the quantity of polysiloxane that will have to be used. For reasons of economy, it is best at to apply a complete coating that is as thin as possible. The quantities of polysiloxane that will be required for a complete
5 coating line between 0.001 and 10 %-wt, mostly between 0.1 and 5 %-wt, relative to the hard material that is used. For the reasons given heretofore, it is preferred that the quantity of polysiloxane that is used during the treatment range between 0.5 and 1.5 per cent by weight relative to the hard material that is
10 used. The quantity used will depend on the grain size or the specific surface area of the grinding grain. The advantageous effect varies very little even if the optimal quantities are exceeded over a relatively large range. The viscosity of the polysiloxane or of the corresponding emulsion or solution that is used should not exceed 1500 mPa*s at room temperature in
15 order to achieve the optimal effect of the coating.

In addition to improved visual properties of the lacquer and laminate coatings, most surprisingly, when the hard material
20 treated according to the present invention was incorporated it was found that the resistance to wear of these layers is higher than comparable layers in which untreated hard material is incorporated. Resistance to wear was determined using the Taber method, whereby a test body is rotated beneath loaded,
25 cylindrical adhesive wheels that are covered with defined abrasive paper and the number of rotations required in order to achieve a specific degree of wear is then measured.

One possible explanation for this surprising effect maybe the good gliding quality and lubricating quality of the polysiloxane. The wear test itself is nothing more than a grinding process and the use of lubricant such as oil when grinding is a generally known technique that is used in order to reduce the coefficient of friction between the material and the grinding agent and thus reduce the aggressiveness of the grinding agent. In the present case it is possible that the effect of the grinding paper is reduced and wear on the lacquer or laminate layer is also reduced.

The present invention will be described in greater detail below on the basis of embodiments without necessarily being restricted to these.

Examples 1 - 5

1 kg pure white corundum (Alodur[®] WSK, Treibacher Schleifmittel), F 280 granulation, was tempered at 400°C and then sprayed with a diluted, aqueous polysiloxane emulsion (Baysilone[®] oil emulsion H, Bayer Leverkusen) when in a drum mixer, after which it was mixed intensively for 20 minutes. The coated granular material was then dried for 20 minutes at 120°C in a convection oven. Subsequently, the total content of SiO₂ and the proportion of polysiloxane on the surface of the grains was determined.

Ex .	Baysilone Oil Emulsion H	Total content SiO ₂ (%-wt)	Content (%-wt) polydimethylsiloxane
1	1 ml in 15 ml H ₂ O	0.032	0.025
2	5 ml in 15 ml H ₂ O	0.135	0.128
3	15 ml (undiluted)	0.589	0.582
4	30 ml (undiluted)	1.309	1.302
5	60 ml (undiluted)	2.743	2.704
6*	0.007		

* untreated comparison material

5 Table 1: Concentration series

The best results in this series were obtained with Example 4. Descriptions were based on electron microscope imagery and measurements of wear values as compared to untreated granular material.

In the Appendix, Illustration 1 shows the untreated granular material (Example 6) with a very finely structured and fissured surface. In comparison to this, Illustration 2 shows the grain surface (Example 4), which is completely covered by the coating according to the present invention. The cracks are closed and have been filled to a large extent. The edges are rounded, and no more edge displacements can be seen. Illustrations 3 and 4 in the Appendix serve to document the effect of the coating according to the present invention on the transparency of a lacquer coating. Whereas the uncoated grains (Example 6) can be clearly seen in the lacquer coating, and a relatively large number of intracrystalline optical refractive edges can be seen, the hard grains coated according to the present invention, shown in Illustration 4, can only be identified poorly by the grain-resin boundary. There are absolutely no intra-crystalline visual refractive edges to be seen.

Table 2 sets out the IP wear values as determined by Draft Standard prEN 13329:1998, Appendix F.

Example	IP Average value from three test bodies	wear resistance compared to untreated grain
1	2200	105%
2	2200	105%
3	2300	109%
4	2500	119%
5	2500	119%
6*	2100	100%

Table 2: Wear values

The test bodies that contained the coated hard grain (Example 4) according to the present invention display enhanced wear resistance that is 19% greater as compared to Example 6.

Illustration 1: Electron micrograph of a surface of untreated
hard grain (Enlargement 3000x)

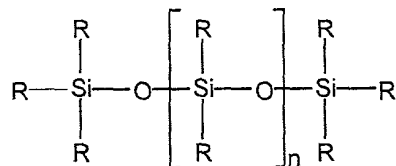
Illustration 2: Electron micrograph of the surface of grain
treated according to the present invention (Enlargement: 3000x)

Illustration 3: Surface of a lacquer coating with untreated hard grains

Illustration 4: Surface of a lacquer coating with hard grains
coated according to the present invention

Patent Claims

1. Surface coated hard material with a hardness (HV_{0.2}) ≥ 10 GPa, the surface of which has a polysiloxane coating.
2. Surface coated hard material as defined in Claim 1, characterized in that the hardness (HV_{0.2}) > 15 GPa.
3. Surface coated hard material as defined in Claim 1 or Claim 2, characterized in that aluminum oxide is the basis of the hard material.
4. Surface coated hard material as defined in Claim 3, characterized in that the basis of the hard material consists of electro-corundum, monocrystalline corundum, sintered corundum, sintered alumina and/or calcined alumina, or mixtures of these.
5. Surface coated hard material as defined in one of the Claims 1 to 4, characterized in that the surface of the hard material is coated with a polysiloxane of the formula:



6. Surface coated hard material as defined in Claim 5, characterized in that the R radical is hydrogen, an alkyl and/or phenyl group.

5 7. Surface coated hard material as defined in Claim 5, characterized in that n is an integer between 1 and 100.

8. Surface coated hard material as defined in one of the Claims 5 to 7, characterized in that the R radical is preferably a methyl group.

10

9. Surface coated hard material as defined in one of the Claims 1 to 8, characterized in that the quantity of polysiloxane on its surface amounts to 0.001 to 10%-wt relative to the hard material that is used.

15

10. Surface coated hard material as defined in Claim 9, characterized in that the quantity of polysiloxane amounts to 0.01 to 5%-wt.

20

11. Surface coated hard material as defined in Claim 9, characterized in that it is preferred that the quantity of polysiloxane amount to 0.1 to 1.5%-wt.

25

12. Method for producing a hard material as defined on one of the Claims 1 to 11, characterized in that a hard material

grain is mixed with a polysiloxane, a polysiloxane emulsion, or a diluted polysiloxane emulsion.

13. Method as defined in Claim 12, characterized in that the
5 hard grain is subjected to a heat treatment in a temperature range between 100°C and 600°C prior to the mixing process.

14. Method as defined in Claim 12 or Claim 13, characterized in
10 that once coated with polysiloxane the hard grain is dried in a temperature range between 100°C and 400°C.

15. Method as defined in Claim 14, characterized in that the
drying temperature is between 100°C and 200°C.

16. Method as defined in one of the Claims 12 to 15,
15 characterized in that an aqueous polysiloxane emulsion is used.

17. Method as defined in one of the Claims 12 to 16,
20 characterized in that the viscosity of the polysiloxane, the polysiloxane emulsion, or the diluted polysiloxane emulsion that is used is below 1500 mPa*s.

18. Method as defined in Claim 17, characterized in that the
25 viscosity of the polysiloxane, the polysiloxane emulsion,

or the diluted polysiloxane emulsion that is used is below
1000 mPa*s.

19. Use of a hard material as defined in one of the Claims 1 to
11 as a wear-reducing agent in lacquer coatings based on
phenol, melamine, aldehyde, urea, formaldehyde, epoxy,
polyester, and/or polyurethane resins.

20. Use of a hard material as defined in one of the Claims 1 to
11 as a wear-reducing agent in transparent overlay papers
to manufacture wear-resistant lacquer coatings.

Abstract

Surface-coated hard material with a hardness ($HV_{0.2}$) ≥ 10 Gpa, the surface of which has a polysiloxane coating. Method for
5 producing this, in which a hard grain is mixed with a polysiloxane, a polysiloxane emulsion, or a diluted polysiloxane emulsion. Use of a hard material of this type as a wear-reducing agent in lacquer coatings.

5

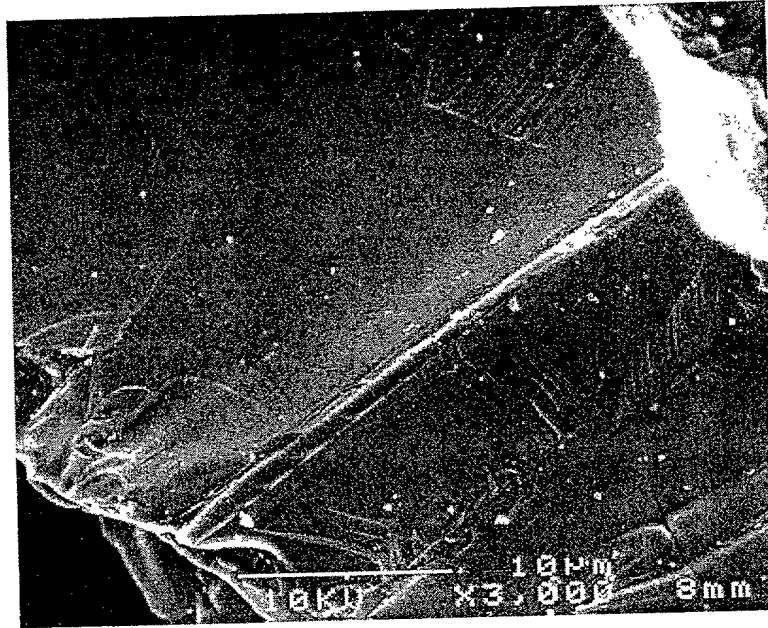


Abbildung 1: REM-Aufnahme einer Oberfläche eines unbehandel-
ten Hartstoffkornes in 3.000-facher Vergrößerung



Abbildung 2: REM-Aufnahme der Oberfläche eines erfindungsgemäß behandelten Korns in 3.000-facher Vergrößerung

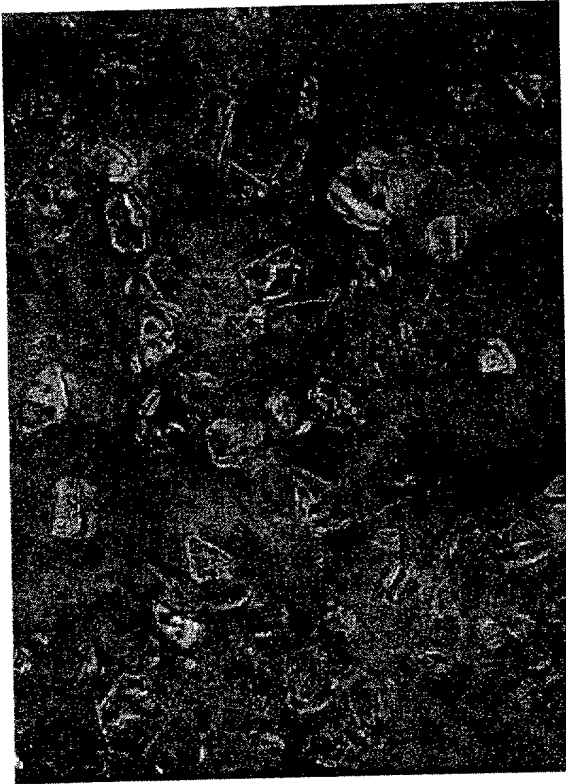


Abbildung 3:

Oberfläche einer Lack-
schicht mit unbehan-
delten Hartstoffkörner

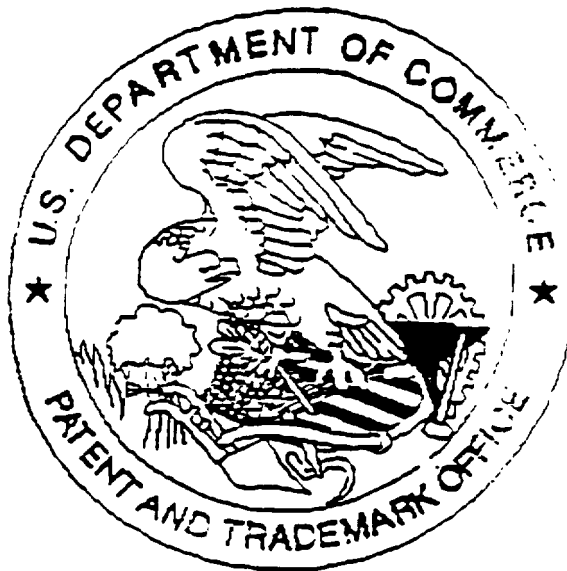
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There are 4 sheets of drawings